Spontaneous Splay of Monolayers Comprised of Chiral Molecules at the Air-Water Interface Due to the Electric Quadrupole Effect

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Spontaneous Splay of Monolayers Comprised of Chiral Molecules at the Air-Water Interface Due to the Electric Quadrupole Effect

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シリンダーモデルを用いて、棒状キラル分子によって構成される水面上単分子膜から発生する自発四重極子モーメント密度を解析した。電気四重極子モーメント密度が発生するためには、分子長軸方向の秩序がなくてはならないことを示した。電気四重極子モーメント密度によって生じる静電エネルギーの解析によって、電気四重極子モーメント密度が単分子膜の自発スプレーの原因になることを示した。

Due to the symmetry breaking of interface, monolayers at the air-water interface form non-centrosymmetric orientational structure. The orientational order parameters $S_n(\equiv \langle\cos\theta\rangle)$ are introduced to represent the orientational structure of monolayers as an extention of the orientational order parameters of liquid crystal S_2 ($P_n(\cos\theta)$:Legendre polynomial). On account of the non-centrosymmetric structure, i.e. $S_1 \neq 0$ and $S_3 \neq 0$, the spontaneous and second order non-linear polarizations are generated from monolayers [1]. We have developed Maxwell displacement current (MDC) and optical second harmonic measurement (SHG) techniques to detect the spontaneous and non-linear polarizations of monolayers comprised of rod-shaped achiral molecules, and measured S_1 and S_3 of monolayers [2]. Recently, the chirality of monolayers comprised of rod-shaped chiral molecules has also been detected by MDC and SHG [3]. Here, we analyze electric quadrupole moment density generated from monolayers comprised of chiral molecules for the further understanding of the dielectric physics of monolayers.

In our previous study [4], the rod-shaped chiral molecules are modeled by cylinders with dipole moment attached at the surface of the cylinder (see Fig.1). This model molecules represent chirality with respect to the molecular long axis and dipole moment. The electrical property of this molecules is expressed by the sum of dipole moment $\mu = \mu(0, \sin\theta_c, \cos\theta_c)$ and electric quadrupole moment $\mathbf{q}_\xi = \mu d_0/2(0, \sin\theta_c, \cos\theta_c))$. The spontaneous quadrupole density generated from monolayers comprised of the model molecules are calculated as

$$\mathbf{Q}_z = \frac{N_s \mu d_0}{2} \begin{pmatrix} \sin\theta_c\langle\sin\theta\cos\psi\cos\phi\cos\theta\sin\psi\rangle - \cos\theta_c\langle\sin^2\theta\cos\psi\cos\phi\rangle \\ -\sin\theta_c\langle\sin\theta\cos^2\psi\cos\phi\rangle \\ -\sin\theta_c\langle\sin^2\theta\cos\psi\sin\psi\rangle - \cos\theta_c\langle\sin\theta\cos\psi\cos\theta\rangle \end{pmatrix}, \quad (1)$$

where θ, ψ, and ϕ are the tilt angle, twist angle, and tilt azimuth, respectively. x and z are parallel to the average in-plane orientational direction of molecular long axis (c-director) and water

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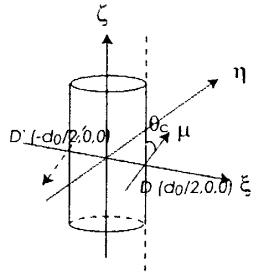

Figure 1: Model of constituent chiral molecules.

surface normal. y is the in-plane direction perpendicular to the in-plane orientational vector. $\langle\rangle$ is the thermodynamic average in terms of the orientational distribution function $f(\theta,\psi,\phi)$. Eq.(1) indicates that the in-plane component of $\mathbf{Q}_z$ is non-zero only when constituent molecules possess orientational ordering with respect to the tilt azimuth, i.e. nematic order. Thus, $\mathbf{Q}_z$ is generated only from monolayers in liquid crystal phases. Under the chiral transformation, i.e. $\theta_c \rightarrow -\theta_c$ and $f(\theta,\psi,\phi) \rightarrow f(\theta,-\psi,-\phi)$, only sign of the y-component of $\mathbf{Q}_z$ changes. In other words, the characteristic of molecular chirality appears in the y-component of $\mathbf{Q}_z$.

On account of $S_1 \neq 0$, the spontaneous polarization $P_{0\perp}$ is generated from monolayers in z direction. The divergence of spontaneous electric quadrupole density is viewed as polarization ($P_z^Q = -\nabla\cdot\mathbf{Q}_z$). Thus, the electrostatic energy is stored due to the interaction between $P_{0\perp}$ and P_z^Q. When the distribution of $\mathbf{Q}_z$ possesses radial symmetry ($\mathbf{Q}_z(\mathbf{r}) = \mathbf{Q}_z(r)$), the electrostatic energy is written as

$$F = -\int_{-\pi}^{\pi} d\theta \int_0^a r' dr' s_0(r') \nabla\cdot\mathbf{Q}_z, \tag{2}$$

where $s_0(r') = \frac{P_{0\perp}}{r'}\int_{r'/a}^1 dt[\frac{8}{(1-t^2)^2}E(t) - \frac{4}{1-t^2}F(t)]$. $F(t)$ and $E(t)$ are the complete elliptic integrals of first and second kind, respectively. In the liquid crystal physics, eq.(2) is nothing but the spontaneous splay. Thus, the interaction between spontaneous polarization and electric quadrupole moment density contributes to the free energy of monolayers as spontaneous splay.

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